ARYLATIONS OF COAL MODEL SYSTEMS

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Currently, coal is converted to clean liquids or low melting solids by processes which utilize high temperature, high pressure, or both. These processes occur by thermal bond cleavages and involve the intermediacy of free radicals. In a search for chemistry which could liquefy coal under milder conditions, we have focussed on thermally less demanding ionic reactions.

Of the functional groups which commonly occur in coals, ethers are the easiest to cleave under acid conditions. Depending on the density of these linkages and their importance as crosslinks in the macromolecular structure of coals, solubilization might be greatly enhanced solely by cleaving and capping ether bonds. Benzylic ethers are particularly reactive and have been implicated in the initiation of coal pyrolysis(1) and hydropyrolysis(2). Arylation, the use of acids to cleave bonds in coals in the presence of aromatic rings to trap the consequent incipient carbonium ions, has a long history(3). The most extensively studied system is the Heredy-Neuworth phenol depolymerization(4).

We have chosen to use benzyl phenyl ether and 1-naphthylmethyl phenyl ether and polymers related to them as models to develop and evaluate the chemistry involved in the arylations.

RESULTS

Arylmethyl phenyl ethers undergo competing reactions when treated with Lewis acids. A partitioning of arylmethyl groups between an intramolecular process (a rearrangement) and an intermolecular one can be seen in Table 1. The fact that the rearranged product is over-whelmingly the ortho isomer is consistent with the intramolecular

$$PhCH_2\text{-}OPh \xrightarrow[\text{Ph-H}]{\text{Acid}} PhCH_2\text{-}Ph + HOPh + \underset{CH_2Ph}{\overset{OH}{\bigcirc}} \qquad (1)$$
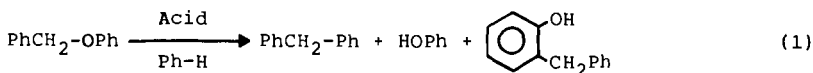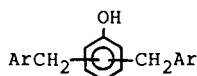
nature of the rearrangement(5). Regardless of the choice of acid or temperature, essentially one-half of the starting phenylmethyl phenyl ether, 1, ends up as rearranged product. Table 2 shows that generally the same result holds for 1-naphthylmethyl phenyl ether, 4. However, a previously unrecognized complication shows up in the products of the acid-catalyzed reaction of 4.

Despite the fact that solvent benzene is in great excess, substrate or product or both, effectively compete for the 1-naphthylmethyl moiety. Capillary gc-ms reveals that at least five products of molecular weight 374 are produced in these reactions. This corresponds to structures containing two 1-naphthylmethyl groups and one phenol. These products can arise by substrate capture of a 1-naphthyl-methyl followed by ether-to-phenol rearrangement or, alternatively, by capture of 1-naphthylmethyl by products 5. Even under conditions where the molar ratio of benzene to starting material
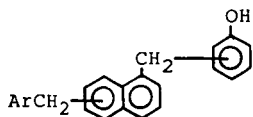
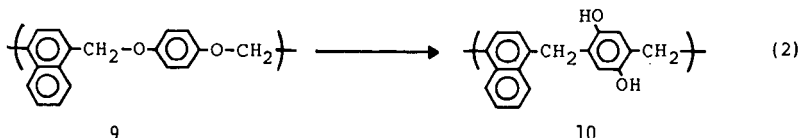21 isomers possible   6 isomers possible

exceeds 1000, a significant number of product molecules derive from more than one molecule of starting ether.

If substrate and/or products can trap the electrophilic 1-naphthylmethyl species with such efficiency, it stands to reason that other aromatic compounds will likely be better than benzene also. Table 3 shows data demonstrating that this is the case. The fact that the relative rate constant measured for the naphthalene-benzene competition remains constant over a 100-fold change in naphthalene concentration, confirms that the change in product slate arises by the simple partitioning of an intermediate between the two traps. The straightforward behavior of the system was further checked by allowing diphenylether and 2,6-dimethylphenol to compete directly. The rate constants determined when three traps are present are sensibly the same as those found in binary competition (see last line of Table 3).
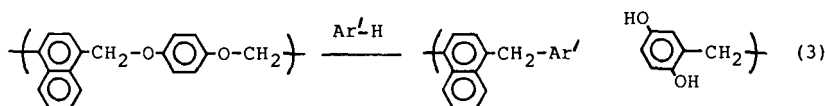
One would expect the same sort of behavior for the trapping of intermediates generated from insoluble materials. Naphthalene should be a substantially better capping agent than benzene. The results of the BF_3-catalyzed arylations of polymer 9 with benzene, naphthalene, or phenanthrene as traps in CH_2Cl_2 solvent are given in Table 4, along with the results from some reactions carried out in benzene solvent.

Of particular importance is the fact that the solubilities of products generated in the presence of naphthalene and phenanthrene differ markedly from that produced by BF_3 treatment alone. Infrared spectra clearly establish that the ether functions present in the starting polymer are no longer present in the products. Apparently, in the absence of a trap, polymer 9 is converted to a new polymer, whose structure is best approximated as 10, equation 2, although we recognize that substantial amounts of interchain crosslinking might occur. The enhanced solubility in the presence of arene, therefore, signals the lowering of molecular weight by capping reactions, equation 3.
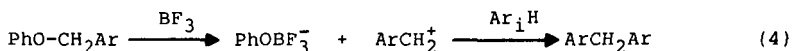

9   10

$$\left(\text{naphthyl-CH}_2\text{-O-}\bigcirc\text{-O-CH}_2 \right) \xrightarrow{\text{Ar}^{\prime}\text{H}} \left(\text{naphthyl-CH}_2\text{-Ar}^{\prime} \right) \quad \overset{\text{HO}}{\underset{\text{OH}}{\bigcirc}}\text{-CH}_2 \quad (3)$$

DISCUSSION

The results reported here are best interpreted on the basis of a model in which carbonium ions generated from arylmethyl phenyl ethers are partitioned between the various nucleophiles present. In this system, aromatic rings are the most nucleophilic functional groups. The 1-naphthylmethyl cation is much more stable than is the simpler

$$\text{PhO-CH}_2\text{Ar} \xrightarrow{\text{BF}_3} \text{PhOBF}_3^- \; + \; \text{ArCH}_2^+ \xrightarrow{\text{Ar}_i\text{H}} \text{ArCH}_2\text{Ar} \qquad (4)$$

benzyl cation, and, consequently, much more selective in its reactivity(6). Thus, in the case of benzyl phenyl ether, 1, solvent benzene effectively traps all generated carbonium ions. However, the more stable 1-naphthylmethyl cation generated from 4, is sufficiently stable to discriminate between the poorly nucleophilic benzene and the more nucleophilic molecules, 4 and 5. Naphthalene, on the other hand, is much more nucleophilic than benzene(7), and in sufficient concentration, suppresses "self-trapping".

The same picture emerges from work with polymer 9. Apparently, benzene is insufficiently reactive to compete with intramolecular (intrapolymer) nucleophiles and, consequently, no increase in solubility accompanies the cleavages of ether links in 9 upon addition of benzene. When better nucleophiles, naphthalene and phenanthene, are provided, carbonium ions generated from ether cleavages <u>are</u> capped and the product is lower in molecular weight and more soluble.

It is worth noting that the naphthalene (k_{rel}=280) is nearly as good a trap as the phenol (k_{rel}=450). Since hydroxylic solvents will level the acid strength of BF_3 to that of $ROBF_3^-H+$ and hydrocarbons would not, the acid-catalyzed bond cleavages necessary for unlinking coal may in fact be faster in BF_3-arene than in BF_3-phenol. While we have not yet extended these results to coals, we believe that the combination of a relatively mild Lewis acid catalyst, BF_3, with a good carbonium ion trap, naphthalene, will allow selective cleavage and capping of aryl alkyl ether bonds.

EXPERIMENTAL

All gas chromatographic (GC) analyses were performed on a Tracor model 550 gas chromatograph with flame ionization dectector; glass columns were 6'x4mm and 6'x2mm, packed with 3% OV-1 or OV-101 on 80-100 mesh supelcoport, respectively. Columns were held at 80°C for 2 min. and then the temperature raised to 275°C at 25°/min and held for 10 min (benzyl phenyl ether reactions) or initially held at 120° and the temperature raised to 200° at 5°/min and held for 10 min (1-naphthylmethyl phenyl ether reactions). Peak areas were integrated by the "cut and weigh" method. NMR spectra were obtained on a Varian EM 360, IR spectra on a Beckman IR-4230 and GC-Mass Spectra on a Finnigan

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4023. Liquid chromatographic analyses were carried out on a Varian 5000 LC with a Varian UV-50 detector at 270 nm.

Benzyl phenyl ether and 1-naphthylmethyl phenyl ether were prepared by reaction of phenoxide ion with the requisite halide, and purified by recrystallization. The polymer 9 has been previously described(8).

Reaction of Arylmethyl Phenyl Ethers with Lewis Acids in Benzene. General Procedure

The arylmethyl phenyl ether, internal standard (hexadecane or dodecane) and trapping agents (naphthalene, 2,6-dimethylphenol or diphenylether) when used, were placed in a dry flask and dissolved in benzene that had been dried by azeotropic distillation and stored over 4A molecular sieves. Lewis Acid (BF_3, BF_3-CH_3OH or $AlBr_3$) was then added as a dilute benzene solution or directly to the reaction mixture at room temperature. Aliquots were removed at timed intervals, quenched with water, and diluted for LC and/or GC analysis.

Reaction of Polymer 9 with Arenes Catalyzed by Lewis Acids

To a dry flask outfitted with a magnetic stirrer was placed polymer, 9, dry solvent (benzene or methylene chloride), and trap (naphthalene or phenanthrene) when used. Lewis acid was added, in most cases, as a dilute solution or, in a few runs with BF_3, as a gas. The heterogeneous mixture was stirred for the indicated time at the required temperature. The resulting blue-green reaction mixture was quenched with water, filtered and washed. The insoluble residue was dried, weighed and analyzed by IR. The organic filtrate was dried and the solvent removed under vacuum.

REFERENCES

1. Siskin, M.; Aczel, T. Fuel 1983, 62, 1321.

2. Tanner, K.I.; Bell, A.T. Fuel 1981, 60, 52.

3. Larsen, J.W.; Kuemmerle, E.W. Fuel 1976, 55, 162.

4. Wender, I.; Heredy, L.A.; Neuworth, M.B.; Dryden, I.G.C. In "Chemistry of Coal Utilization. Second Supplementary Volume"; Elliott, M.A., Ed.; Wiley: New York, 1981; Chapter 8, pp. 447-454; and references therein.

5. Dewar, M.J.S. In "Molecular Rearrangements, Part 1"; de Mayo, P., Ed.; Wiley: New York, 1963; Chapter 5.

6. Streitwieser, A., Jr. Chem. Rev. 1956, 56, 571.

7. Dewar, M.J.S.; Mole, T.; Warford, E.W.T. J. Chem. Soc. 1956, 3581, report k(naphthalene)/k(benzene)=350 for nitration.

8. Squires, T.G.; Smith, B.F.; Winans, R.E.; Scott, R.G.; Hayatsu, R. Proc. Intern. Conf. Coal Sci. 1983, 292.

9. Bunnett, J.F. In "Investigations of Rates and Mechanisms of Reactions"; Lewis, E.S., Ed.; Wiley-Interscience: New York, 1974; Chapter IV, pp. 158 ff.

Table 1. Products of Acid-catalyzed Phenylation of Phenyl Benzyl Ether.[a]

$$Ph-CH_2O-Ph \xrightarrow[Ph-H]{Acid} PhCH_2-Ph + HO-Ph +$$

1	2	3
	intermolecular	intramolecular

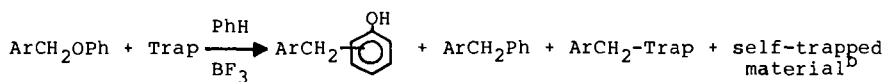| ACID	Ph_2CH_2	o-benzylphenol
CF_3SO_3H	44%	48%
$BF_3 \cdot CH_3OH$	47%	40%
$BF_3 \cdot CH_3OH$ (72°)	49%	49%
BF_3	49%	48%
$AlBr_3$	48%	54%

[a] Room temperature, benzene solvent.

Table 2. Products of BF_3-Catalyzed Cleavage of 1-Naphthylmethyl Phenyl Ether.[a]

$$ArCH_2OPh \xrightarrow[BF_3]{PhH} ArCH_2 \text{—} \underset{OH}{\bigcirc} + ArCH_2Ph + PhOH + \text{"self trapped material"}$$

4	5	6	7

$ArCH_2OPh$	o-5	p-5	6	recovery	7[b]
0.2M	30	12	<1	43%	(1.00)
0.02M	37	15	6	58%	.76
0.002M	50	16	12	78%	.27

[a] Room temperature, benzene solvent

[b] Relative yield of several products from liquid chromatographic analysis.

Table 3. Relative Trapping Ability of Aromatic Compounds in BF$_3$-Catalyzed Cleavage of 1-Naphthylmethyl Phenyl Ether.[a]

$$\text{ArCH}_2\text{OPh} + \text{Trap} \xrightarrow[\text{BF}_3]{\text{PhH}} \text{ArCH}_2\text{-}\underset{}{\text{C}_6\text{H}_4\text{OH}} + \text{ArCH}_2\text{Ph} + \text{ArCH}_2\text{-Trap} + \text{self-trapped material}^b$$

		5		6	8	7
Trap	Trap , M	o-5	p-5	6	8	k$_{rel}$[c]
Benzene	0	38	13	7	--	(1)
Naphthalene	.020	33	14	7	3	280
Naphthalene	.20	37	14	3	17	310
Naphthalene	2.0	32	8	1	46	260
Diphenyl Ether	.20	41	13	4	4	50
2,6-Dimethylphenol	.20	39	12	2	17	450
Diphenyl Ether	.20	28	9	1.5	15	500
2,6-Dimethylphenol	.20				1.3	45

[a]Room Temperature, benzene solvent.

[b]See Figure 1 for relative yields of self-trapped material.

[c] $\dfrac{k_{trap}}{k_{PhH}} = \dfrac{[\text{ArCH}_2\text{-Trap}]}{[\text{ArCH}_2\text{Ph}]} \times \dfrac{[\text{PhH}]}{[\text{Trap}]}$, see reference 9.

Table 4. BF$_3$-Catalyzed Arylation of Polymer 9.

			Product solubilities[a]		
ArH/solvent	Acid	Temp.	CH$_2$Cl$_2$	PhH	Acetone
CH$_2$Cl$_2$	BF$_3\cdot$H$_2$O	23°			0%[b]
CH$_2$Cl$_2$	BF$_3$	20°	<5%		
PhH/CH$_2$Cl$_2$[c]	BF$_3$	20°	<5%		
naphthalene/CH$_2$Cl$_2$[c]	BF$_3$	20°	29%		
phenanthrene/CH$_2$Cl$_2$[c]	BF$_3$	20°	24%		
PhH	BF$_3\cdot$CH$_3$OH	80°		11%	39%
PhH	BF$_3$	23°		19%	76%

[a]Determined by weight of insoluble product.

[b]IR shows complete loss of ether functionality.

[c]0.4 M Arene.

ACKNOWLEDGEMENT
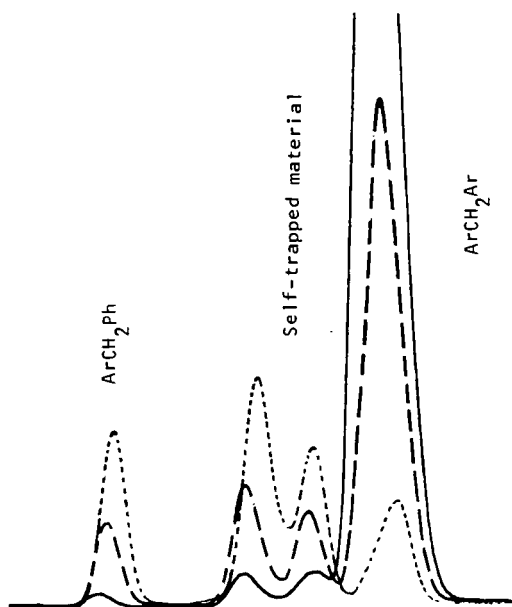
Figure 1. Liquid Chromatograms of the
Naphthylation of 1-Naphthylmethyl Phenyl
Ether, $ArCH_2OPh$ (see Table 3).

········ 0.020 M Naphthalene (ArH)

-------- 0.20 M Naphthalene (ArH)

————— 2.0 M   Naphthalene (ArH)